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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US85/00527 (22) International Filing Date: 28 March 1985 (28.03.85) (31) Priority Application Number: 594,609 (32) Priority Date: 29 March 1984 (29.03.84) (33) Priority Country: US (60) Parent Application or Grant (63) Related by Continuation US 594,609 (CIP) Filed on 29 March 1984 (29.03.84) (71) Applicant (for all designated States except US): AMERICAN HOECHST CORPORATION [US/US]; Route 202-206 North, Somerville, NJ 08876 (US).		(72) Inventors; and (75) Inventors/Applicants (for US only) : VAN DELINDER, George, S. [US/US]; 299 Page Street, Lunenburg, MA 01462 (US). NALEPA, Raymond [US/US]; 339 Day Street, Leominster, MA 01453 (US). COLFORD, Donald [US/US]; 3 Robin Lane, Hingham; MA 02043 (US). (74) Agents: BLASKO, John, P. et al.; American Hoechst Corporation, Patent Department, Route 202-206 North, Somerville, NJ 08876 (US). (81) Designated States: DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, US. Published <i>With international search report.</i>

(54) Title: POLYETHYLENE MOLDING COMPOSITION AND PROCESS



UNMODIFIED POWDER 5000X

(57) Abstract

Novel ultra high molecular weight polyethylene molding composition and a process for preparing and using said composition. The product of this invention is particularly suited for making porous, plastic products by the free-sintering method. The product of this invention is prepared by compacting powdered ultra high molecular weight polyethylene under the influence of pressure and heat to alter the morphology and molding characteristic of the material.

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"POLYETHYLENE MOLDING COMPOSITION AND PROCESS"

Background of the Invention

It is well known in the art to prepare porous articles from thermo-plastic polymers. In particular, it is known to prepare porous polyethylene products from a polymer having a molecular weight in excess of 1×10^6 ; such polyethylenes are referred to as ultra-high molecular weight polyethylene and are readily available.

Porous ultra-high molecular weight polyethylene is useful in many applications, e.g., filters, pen tips, noise dampers, diffuser plates, battery separators, etc. This polyethylene has excellent physical properties, e.g., abrasion resistance, low coefficient of friction and toughness even at low temperatures.

Although ultra-high molecular weight polyethylene possesses many outstanding physical properties, it does not flow well under the influence of heat and pressure. Ultra-high molecular weight polyethylene is very viscous above its melting point and undergoes substantial shear degradation under the influence of the mechanical forces usually encountered in extrusion and injection molding processes.

In the field of porous products, it is not uncommon to encounter finished parts that are weak and brittle. We feel that the high melt viscous and the particle morphology of the ultra-high molecular weight polyethylene influence the strength of the molded porous part. It is the object of this invention to overcome this problem of poor moldings by altering the particle morphology.

Porous plastic products may be prepared by the free

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sintering of a polyethylene powder in a closed mold. Various prior art references are available disclosing other methods for the preparation of porous products from ultra-high molecular weight polyethylene e.g., see U.S. Patent No. 3,051,993 and No. 3,954,927.

Also the prior art discloses that the molding characteristics of ultra-high molecular weight polyethylene can be improved by heat treating the ultra-high molecular weight polyethylene powder prior to compression molding, see for example U.S. Patent No. 4,246,390. It is also taught in the prior art that ultra-high molecular weight polyethylene could be screw-injection molded if the powdered polymer was first formed into a pellet, see for example South African Patent No. 81/3915.

Brief Summary of the Invention

We have discovered that strong flexible porous products may be prepared from a compacted ultra-high molecular weight polyethylene powder. The compacted ultra-high molecular weight powder of this invention is prepared by (1) compacting the powder by application of an effective amount of pressure and heat to increase its bulk density and to substantially reduce the particle's "fine structure", e.g., by passing the powder through a pellet mill or a roll mill; and (2) if necessary, dispersing and classifying the compacted powder into powder having a particle size suitable for preparing porous products.

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Description of Figures

Figures 1 - 6 are scanning electron micrographs of an unmodified ultra-high molecular weight polyethylene powder at magnifications of 100; 250; 500; 750 and 1500 respectively as identified on the figures.

Figures 7 - 12 are scanning electron micrographs of ultra-high molecular weight polyethylene powder according to this invention of magnifications of 100, 250 (sinstered), 500, 750 (sinstered), 1500 (sinstered), and 5000 respectively designated on the figures.

Description of the Invention

The following terms and test procedures are used in this description.

Ultra-high molecular weight polyethylene (sometimes abbreviated as UHMW polyethylene) means a polyethylene having a molecular weight of about 1×10^6 or more as determined from the intrinsic viscosity of the material in decalin at 135°C in accordance with the following formula:

$$MW = 5.37 \times 10^4 (\text{intrinsic viscosity})^{1.49}$$

The weight average molecular weight values reported herein were determined in accord with ASTM D 4020-81 at a polymer concentration of 0.03 weight.

The sieve analysis and stiffness values reported herein were determined in accord with the ASTM D-1921-63 test method and the ASTM D-74-70 test method using a 1.0 in.-lb. load, respectively.

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The bulk density, or mass per unit volume of a material, was measured according to two methods. "Loose bulk density" is determined by gently filling a 100 ml capacity measuring beaker with the molding powder and leveling off any accumulated heap of powder with a piece of cardboard at an angle of 45°. The difference in weight of the filled and empty beaker is established to the nearest 0.1 gram and divided by 100 to give bulk density units (g/ml). The results are equivalent to those of the ASTM D-1895-69 method within a standard deviation of ± 0.012 bulk density units. The "packed bulk density" of a molding powder is determined in the same manner as loose bulk density except that the measuring beaker is tapped lightly on its side as the powder is added in order to settle it. When the powder will not settle any further and the beaker is filled and leveled, the full beaker is weighed and the packed bulk density is calculated.

The percent or degree of porosity was determined or calculated using the following formula:

$$\text{Porosity \%} = (1 - D_s/D_p) \times 100$$

D_s = density of molded sample

D_p = density of polyethylene = 0.94.

This invention is that of a compacted ultra-high molecular weight polyethylene powder having improved molding properties and which is particularly adapted for the preparation of porous products. The ultra-high molecular weight polyethylene of this invention is prepared by compacting unmodified ultra-high molecular weight polyethylene powder in a

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suitable device. The pressure and heat resulting from compacting alters the morphology of powder by substantially reducing the particles' "fine structure" and increases its bulk density value; see for example Figure 1 in comparison to Figure 7, and Figure 6 versus Figure 12; see also Table I, bulk density values.

Typical compacting devices are a pellet mill, a roll press or a tableting press. The unmodified ultra-high molecular weight polyethylene may be compacted into predetermined particle size suitable for direct molding into a porous part or it may be compacted into a larger particle, which is ground and classified into the desired particle size range.

EXAMPLE I

An unmodified ultra-high molecular weight polyethylene powder produced by polymerization using a coordination catalyst system was compacted and pressed into about 1/4 inch x 1/4 inch pellets on a pellet mill. In the pellet mix, the unmodified powder was fed into the interior of a rotating circular die. Adjacent the interior perimeter of the die were located a pair of rollers mounted on fixed axes. These rollers force the powder through the holes provided in the rotating die. The compressed powder forms a number of strands which are cut into pellets by a fixed knife blade proximate the exterior surface of the die.

The pelletizing step creates an amount of frictional heat which may not dissipate. In that case, water can be sprayed on

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or mixed with the powder before it is compressed. Excess moisture can be removed from the pellets by air drying on a screen.

After the pellets were obtained they were broken in a Henschel type mixer by mixing them for two minutes. The disintegrated pellets were then passed over an 18-mesh size screen to remove large particles which were recycled to mixer for further grinding.

EXAMPLE II

The screened modified powder was then placed in an eight-cavity, aluminum compression mold. The dimension of each cavity was 1/4" width x 1-1/2" length and 1/8" depth. The mold was tapped several times to ensure good packing and leveled with additional powder. Excess powder was screened from the mold with a straight-edge and the cover was placed on the mold. The filled mold was placed between press plattens which had been preheated to 375°F and 5 - 10 psig pressure was placed on the plattens to close the mold. After twelve (12) minutes, the mold was removed from the press and cooled by slowly flooding the exterior of the mold with water. After cooling the mold, the test strips were removed from the cavities and air cooled for 24 hours.

EXAMPLE III

Unmodified ultra-high molecular weight polyethylene powder was molded into test specimens using the procedure set forth in Example II.

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The properties of the ultra-high molecular weight polyethylene powder and molded test specimens are reported below in Table I.

<u>Table I</u>		
	<u>Example 3</u>	<u>Example 2</u>
	<u>Unmodified Powder</u>	<u>Modified Powder</u>
Bulk Density g/cc Packed	0.44	.60
Wt. Avg. Mole. Wt:	2.4×10^6	2.4×10^6
Sieve Analysis:		
>1.0 mm %	0.1	--
>0.5 mm %	1.2	7.9
>0.25 mm %	1.9	6.7
>0.125 mm %	33.9	60.4
>0.063 mm %	58.0	23.6
<0.063 mm %	4.9	1.4
Stiffness psi:	480	2107.4
Degree of Porosity %	48	39

The results of Examples II and III show that the stiffness of the molded part as determined by ASTM D-747-70 using a 1.0 pound load increased by over three hundred percent with only a nine percent drop in porosity.

The modified polyethylene powder of the invention can have a particle size distribution predominately in the range of 0.25 mm to about 0.063 mm. Approximately ninety percent of the material may have a particle size between 0.063 mm to 0.25 mm. At least fifty percent of the powder should have a particle

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size within this range. Preferably seventy percent by weight of the molding powder may have a particle size of about 0.25 mm to 0.063. Preferably the molding composition of the invention contains less than one percent by weight of particles having a diameter greater than 1.0 mm and no substantial portion of the composition with a particle size less than 0.038 mm.

EXAMPLE IV

A quantity of unmodified ultra-high molecular weight polyethylene powder was screened and found to have a particle size distribution of about 86.1 percent of the particles within the range of 0.063 mm to 0.25 mm. The powder was molded into test specimens according to the procedure set forth in Example II. The properties of the molding powder and the molded test specimens are reported in Column A of Table II.

In a similar manner, another sample of unmodified UHMW polyethylene powder was analyzed and molded into test specimens. The sieve analysis showed that 55.5 percent of the sample had a particle size distribution between 0.063 mm and 0.25 mm. The results of the testing of this sample are reported in Column B of Table II.

Finally, a quantity of UHMW polyethylene powder was modified according to the process set forth in Example I and molded in accordance with the procedure of Example II. The modified powder was found to have a particle size distribution of 43.1 percent in the range of 0.063 mm to 0.25 mm. The properties of this sampling are set forth below in Column C of Table II.

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Table II

	A	B	C
	<u>Unmodified Powder</u>	<u>Unmodified Powder</u>	<u>Modified Powder</u>
Bulk Density			
Packed g/cc	0.43	0.42	0.48
Loose g/cc	0.39	0.38	0.41
Sieve Analysis			
>0.5 mm %	0.1	0	42.5
>0.25 mm %	13.7	44.5	14.3
>0.125 mm %	84.1	54.7	39.8
>0.063 mm %	2.0	0.8	3.3
Pan %	0.1	0	0.1
Particle Size Distribution			
0.063-0.25 mm %	86.1	55.5	43.1
Stiffness psi	1366	819	805
Relative Solution Viscosity	40.3	--	35.0

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EXAMPLE V

Unmodified ultra-high molecular weight polyethylene powder was molded according to the procedure of Example II. A portion of the powder was then modified in accordance with the process of Example I and subsequently molded. The properties of the modified and unmodified powder and the molded specimens are set forth below in Table III.

Table III

		A	B
		<u>Unmodified Powder</u>	<u>Modified Powder</u>
Bulk Density			
Packed	g/cc	0.44	0.50
Loose	g/cc	0.39	0.42
Sieve Analysis			
>0.5	mm %	0.1	0.2
>0.25	mm %	0.8	0.8
>0.125	mm %	51.5	63.4
>0.063	mm %	44.8	31.9
>0.038	mm %	2.6	3.5
Pan	%	0.3	0.2
Particle Size Distribution			
0.063-0.25	mm %	95.3	95.3
Stiffness	psi	281	1761

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EXAMPLE VI

A quantity of unmodified ultra-high molecular weight polyethylene powder was analyzed and then molded according to the procedure of Example II. The properties of the powder and the molded specimens are set forth below in Column A of Table IV.

A portion of the unmodified powder was pelletized while the die of the pelletizer was below normal operating temperature and the amount of frictional heat was low. Heat stabilizer was added at a concentration of 0.1 percent. The pellets were then broken and screened. The resulting modified powder was molded. The properties of the modified powder and molded specimens are set forth in Column C of Table IV.

Similarly, another quantity of unmodified ultra-high molecular weight polyethylene powder was pelletized, broken apart and screened. However, in this run the pelletization took place under normal conditions while the die was at operating temperature and there was an effective amount of frictional heat present. No heat stabilizer was added during pelletization. The modified powder was molded according to Example II and the properties of the powder and molded specimens are presented in Column D of Table IV.

Still another quantity of unmodified powder was pelletized while the die was at operating temperature, but this time a heat stabilizer was added at a concentration of 0.1 percent. The pellets were again broken apart, screened and then molded. The properties of the modified powder from this sample and the molded specimens are set forth in Column E of Table IV.

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Finally, a sample of unmodified ultra-high molecular weight polyethylene powder was screened and artificially induced to have a particle size distribution approximately the distribution of the modified sample of Column E. The unmodified powder was molded using the procedure set forth in Example II. The properties of the powder and molded specimens of this sample are reported in Column B of Table IV.

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Table IV

		<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Bulk Density						
Packed	g/cc	0.49	0.51	0.56	0.59	0.66
Loose	g/cc	0.43	0.45	0.48	0.52	0.58
Screen Analysis						
>0.5	mm %	0.7	1.5	11.9	11.1	10.0
>0.25	mm %	2.1	7.9	8.6	9.1	8.2
>0.125	mm %	37.4	25.2	22.6	51.0	24.8
>0.063	mm %	55.1	58.9	49.8	25.2	49.6
Pan	%	4.8	6.6	7.2	3.6	7.3
Particle Size Distribution						
0.063-0.25	mm %	92.5	84.1	72.4	76.2	74.4
Stiffness	psi	1092	739	2914	3034	3358
Relative Solution Viscosity		19.3	19.3	--	17.7	17.3

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The surface morphology of the modified polyethylene powder of this invention is markedly changed over the morphology of the unmodified powder. A change in surface morphology was also noted and disclosed by Seaver in his U.S. Patent 4,246,390. However, simply treating the UHMW powder according to Seaver did not produce the superior molding composition of this invention.

The surface of the unmodified UHMW polyethylene powder is characterized by a complex irregular surface structure, see e.g. Figure 5. This complex structure consists of nodules of spherules of less than about 1 micron, crevices and fibrous structure which is termed "fine structure".

Lurie's South African patent 81/3915 discloses a method for compacting UHMW polyethylene powder into pellets. However, he did not recognize the advantages of a compacted powder. Lurie's disclosure teaches, like Seaver, that the "fine structure" of the UHMW polyethylene powder should be substantially reduced and, as can be seen by comparing Figure 6 (untreated powder) with Figure 12 (treated powder), this reduction in fine structure is observed in the products of this invention. In the Lurie patent the combination of heat and pressure is believed to cooperate to compact the UHMW polyethylene powder into a pellet. It is our belief that this combination (i.e. heat and pressure) is required to produce the novel molding powders of this invention. We feel that heat, whether produced by the frictional compression of the UHMW polyethylene powder or externally applied and pressure are required to compact the particles. Generally UHMW polyethylene powders have a bulk density of less than 0.5 grams per cubic centimeter while the

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product of our invention has a bulk density greater than 0.5 gm/cc, preferably greater than 0.55 gm/cc.

The effective amount of pressure and temperature required to produce the novel composition of this invention can easily be determined by simple experimentation. It will be readily understood by one skilled in the art in light of this disclosure that, within reasonable limits, the use of lower pressure can be compensated by the use of a higher temperature or lower temperature compensated by higher pressure. The effective amount of pressure and temperature will also vary with the equipment and residence time. It is always readily understood that stabilizers can be used in the process of this invention to prevent degradation of the polymer.

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WE CLAIM:

1. A molding composition comprising an ultra-high molecular weight compacted polyethylene powder having a packed bulk density equal to or greater than about 0.5 gm/cc, a particle size of about 1.0 mm or less wherein about 50 percent of said composition has a particle size of about 0.25 mm or less and wherein said particles have a surface that is substantially free of fine structure.
2. A molding composition according to Claim 1 wherein the bulk density of said powder is greater than about 0.55 gm/cc.
3. A molding composition according to Claim 1 wherein said bulk density is greater than 0.6 gm/cc.
4. A molding composition according to Claim 1 wherein about seventy percent by weight of said particles have a particle size of about 0.25 mm or less.
5. A molding composition according to Claim 2 wherein about seventy percent by weight of said particles have a particle size of about 0.25 mm or less.
6. A molding composition according to Claim 3 wherein about seventy percent by weight of said particles have a particle size of about 0.25 mm or less.
7. A method of preparing an improved molding composition comprising subjecting UHMW polyethylene powder to an effective amount of heat and pressure so as to increase its bulk density and to substantially eliminate any fine structure of the surface of the powder wherein the particle size of said powder is less than about 1.0 mm.

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8. The method of Claim 7 wherein the packed bulk density is increased to at least 0.5 gm/cc.

9. The method of Claim 7 wherein said packed bulk density is increased to at least 0.55 gm/cc.

10. The method of Claim 7 wherein said packed bulk density is increased to at least 0.6 gm/cc.

11. The method of Claim 7 wherein about fifty percent by weight of said particles have a particle size of about 0.25 mm or less.

12. The method of Claim 11 wherein the packed bulk density is increased to at least 0.5 gm/cc.mm or less.

13. The method of Claim 11 wherein the packed bulk density is increased to at least 0.55 gm/cc.

14. The method of Claim 11 wherein the packed bulk density is increased to at least 0.6 gm/cc.mm.

15. A porous product prepared by sintering an ultra-high molecular weight polyethylene powder having a packed bulk density of at least 0.5 gm/cc.mm, a particle size not greater than about 1.0 mm wherein about fifty percent by weight of said particles have a particle size of about 0.25 mm or less and wherein the surface of said powder is substantially free of fine structure prior to sintering.

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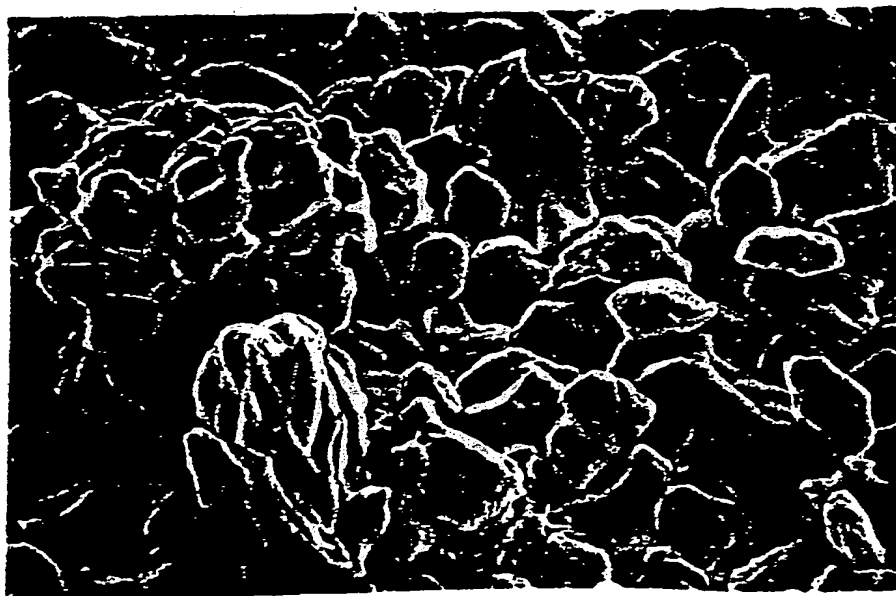


FIG. 1 MODIFIED POWDER 100X



FIG. 2 MODIFIED POWDER, SINTERED 250X

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FIG. 3 MODIFIED POWDER 500X



FIG. 4 MODIFIED POWDER, SINTERED 750X

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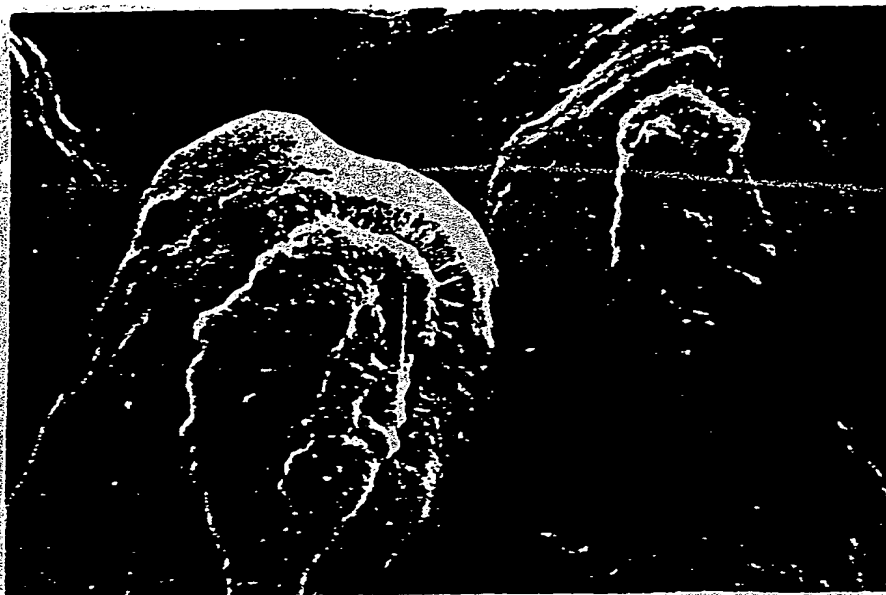


FIG. 5 MODIFIED POWDER, SINTERED 1500X



FIG. 6 MODIFIED POWDER 5000X

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FIG. 7 UNMODIFIED POWDER 100X

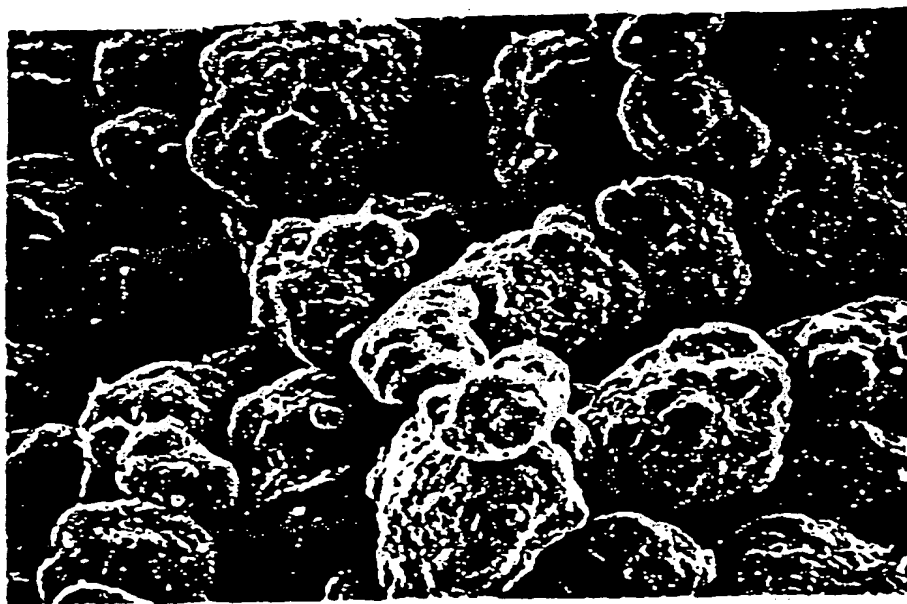


FIG. 8 UNMODIFIED POWDER, SINTERED 250X

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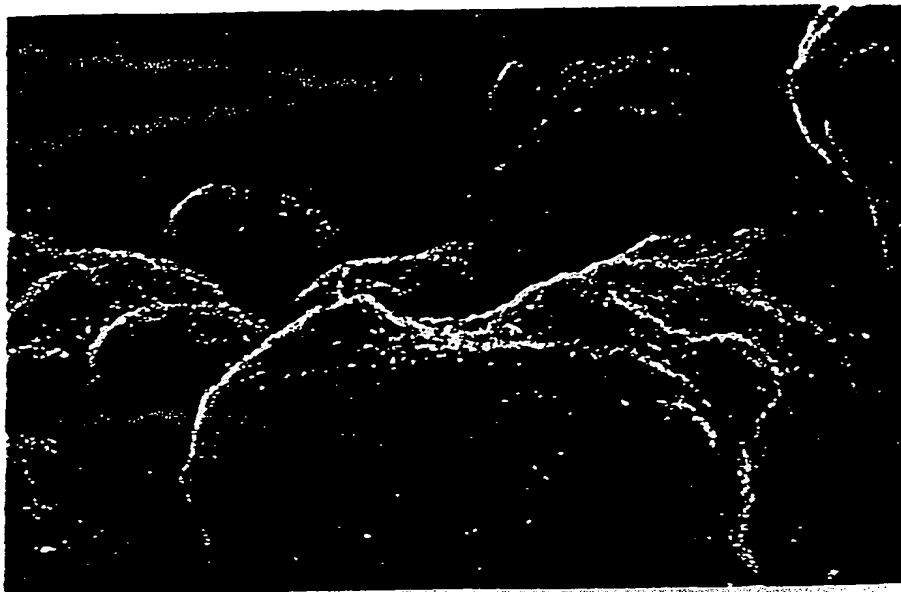


FIG.9 UNMODIFIED POWDER 500X



FIG.10 UNMODIFIED POWDER, SINTERED 750X

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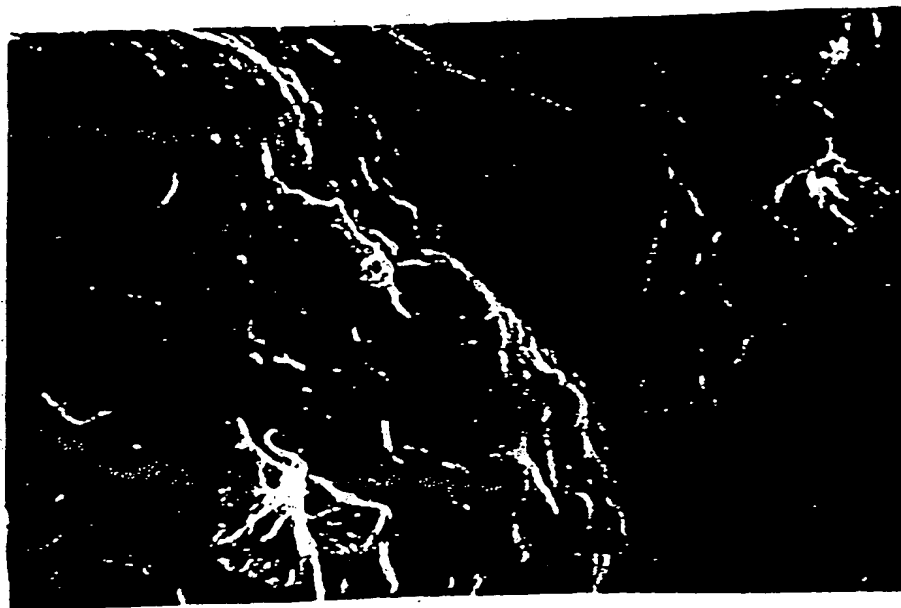


FIG.11 UNMODIFIED POWDER, SINTERED 1500X



FIG.12. UNMODIFIED POWDER 5000X

INTERNATIONAL SEARCH REPORT

International Application No PCT/US85/00527

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³ According to International Patent Classification (IPC) or to both National Classification and IPC ⁴ IPC B29J 5/00; B32B 5/16, 9/00, 15/02, 19/00, 21/02, 17/02, 23/02, 27/02; U.S. CL. 428/402; 264/109																																						
II. FIELDS SEARCHED <div style="text-align: center; border: 1px solid black; padding: 2px;">Minimum Documentation Searched ⁴</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%; border: 1px solid black; padding: 2px;">Classification System</th> <th style="border: 1px solid black; padding: 2px;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; padding: 5px; vertical-align: top;">U.S.</td> <td style="border: 1px solid black; padding: 5px;">428/402 264/15, 109, 118, 126, 331.17 528/502, 503</td> </tr> </table> <p style="text-align: center; font-size: small;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁵</p>			Classification System	Classification Symbols	U.S.	428/402 264/15, 109, 118, 126, 331.17 528/502, 503																																
Classification System	Classification Symbols																																					
U.S.	428/402 264/15, 109, 118, 126, 331.17 528/502, 503																																					
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; padding: 2px;">Category ⁶</th> <th style="width: 70%; padding: 2px;">Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷</th> <th style="width: 20%; padding: 2px;">Relevant to Claim No. ¹⁸</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X, Y</td> <td>US, A, 4,246,390 (SEAVAR) 20 JANUARY 1981</td> <td style="text-align: center; vertical-align: top;">1-15</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 3,051,993 (GOLDMAN ET AL) 04 SEPTEMBER 1962</td> <td style="text-align: center; vertical-align: top;">1-15</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 3,229,002 (FEDER) 11 JANUARY 1966 Col. 2, lines 4-14, 22-46 and Col. 3, lines 55 on.</td> <td style="text-align: center; vertical-align: top;">1-15</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 3,822,177 (MOKED) 02 JULY 1974</td> <td style="text-align: center; vertical-align: top;">1-15</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 3,944,536 (LUPTON ET AL) 16 MARCH 1976</td> <td style="text-align: center; vertical-align: top;">1-15</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 3,954,927 (DULING ET AL) 04 MAY 1976</td> <td style="text-align: center; vertical-align: top;">1-15</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 3,975,481 (BAUMGAERTNER) 17 AUGUST 1976</td> <td style="text-align: center; vertical-align: top;">1-15</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 4,110,391 (BERZEN ET AL) 29 AUGUST 1978</td> <td style="text-align: center; vertical-align: top;">1-15</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 4,171,338 (MASON) 16 OCTOBER 1979</td> <td style="text-align: center; vertical-align: top;">1-15</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 4,248,819 (MAYER ET AL) 03 FEBRUARY 1981</td> <td style="text-align: center; vertical-align: top;">1-15</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 4,272,474 (CROCKER) 09 JUNE 1981</td> <td style="text-align: center; vertical-align: top;">1-15</td> </tr> </tbody> </table>			Category ⁶	Citation of Document, ¹⁵ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸	X, Y	US, A, 4,246,390 (SEAVAR) 20 JANUARY 1981	1-15	Y	US, A, 3,051,993 (GOLDMAN ET AL) 04 SEPTEMBER 1962	1-15	Y	US, A, 3,229,002 (FEDER) 11 JANUARY 1966 Col. 2, lines 4-14, 22-46 and Col. 3, lines 55 on.	1-15	Y	US, A, 3,822,177 (MOKED) 02 JULY 1974	1-15	Y	US, A, 3,944,536 (LUPTON ET AL) 16 MARCH 1976	1-15	Y	US, A, 3,954,927 (DULING ET AL) 04 MAY 1976	1-15	Y	US, A, 3,975,481 (BAUMGAERTNER) 17 AUGUST 1976	1-15	Y	US, A, 4,110,391 (BERZEN ET AL) 29 AUGUST 1978	1-15	Y	US, A, 4,171,338 (MASON) 16 OCTOBER 1979	1-15	Y	US, A, 4,248,819 (MAYER ET AL) 03 FEBRUARY 1981	1-15	Y	US, A, 4,272,474 (CROCKER) 09 JUNE 1981	1-15
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </div> </div>																																						
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search ¹ <div style="text-align: center; font-size: large;">31 MAY 1985</div> </td> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report ¹ <div style="text-align: center; font-size: large;">20 JUN 1985</div> </td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;"> International Searching Authority ¹ <div style="text-align: center; font-size: large;">ISA/US</div> </td> <td style="border: 1px solid black; padding: 5px;"> Signature of Authorized Officer ¹⁰ <div style="text-align: center;"> S. BABAJKO </div> </td> </tr> </table>			Date of the Actual Completion of the International Search ¹ <div style="text-align: center; font-size: large;">31 MAY 1985</div>	Date of Mailing of this International Search Report ¹ <div style="text-align: center; font-size: large;">20 JUN 1985</div>	International Searching Authority ¹ <div style="text-align: center; font-size: large;">ISA/US</div>	Signature of Authorized Officer ¹⁰ <div style="text-align: center;"> S. BABAJKO </div>																																
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FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter ¹³ not required to be searched by this Authority, namely:

2. ☐ Claim numbers because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ¹¹

This International Searching Authority found multiple inventions in this international application as follows:

I. A MOLDING COMPOSITION: CLAIMS 1-6.

II. A METHOD OF PREPARING AN IMPROVED MOLDING COMPOSITION:
CLAIMS 7-14

III. A POROUS PRODUCT: CLAIM 15

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☒ No protest accompanied the payment of additional search fees.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No ¹⁸
Y	US, A, 4,323,531 (BRADLEY ET AL) 06 APRIL 1982	1-15
Y	US, A, 4,436,682 (KNOPP) 13 MARCH 1984	1-15
Y	ZA, 103,915-A (LURIE) JULY 1982	1-15
A	DT, A, 2526-958 (DuFONT) 02 JANUARY 1976	
A	US, A, 3,847,888 (BAUMGAERTNER) 12 NOVEMBER 1974	